1. Introduction

Electron spin resonance (ESR), also known as electron paramagnetic resonance (EPR), refers to the phenomenon of a resonance transition occurs between magnetic energy levels when the electron spin magnetic moment is affected by an electromagnetic wave of specified frequency in a magnetic field. This phenomenon can be observed in paramagnetic substances with unpaired spin magnetic moment, such as (1) atoms with odd number of electrons, e.g. Hydrogen atom; (2) ions of not fully filled with electrons in inner electronic shell layer, e.g. ions of transition elements; (3) molecules with odd number electrons, e.g. NO; (4) molecules with non-zero total angular momentum, e.g. O_2; (5) free radicals generated in reaction process or by exposing to radiation; (6) unpaired electrons in semiconductors, and so on. Therefore, electron spin resonance is an important method to acquire the micro-structure of substances through probing the unpaired electrons in the material and analyzing how they interact with the surrounding atoms. This method has high sensitivity and resolution, and it is a non-destructive detection technique widely used in physics, chemistry, biology and medicine, and other fields of study.

This system of ESR in microwave band is a specially designed teaching apparatus. It is easy-to-use, stable, and reliable for modern physics experiments and research projects.

2. Theory

A. Experimental Sample

The sample provided in this experiment is an organic compound containing free radical, DPPH (Di-phenyl-picryl-Hydrazyl) with a molecular formula of $(C_6H_5)_2N\text{-}NC_6H_2(NO_2)_3$. Its structure is shown in Figure 1.

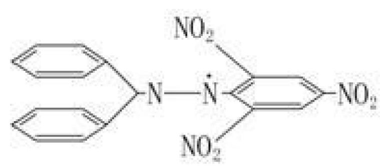

Figure 1 Molecular structure of DPPH

The second *N* atom lacks a covalent bond, or has an unpaired electron or "free electron". It is a stable organic free radical with only spin angular momentum, but lacks orbital angular momentum. In other words, the total orbital angular momentum is fully quenched. So, the ESR phenomenon can be easily observed. As the “free electron” is not completely free, the standard value of *g*-factor is 2.0036 and the standard line width is 2.7×10^{-4} T.

B. Comparison of ESR and NMR

Electron spin resonance (ESR) is used to study the resonance transition phenomenon between unpaired electrons while nuclear magnetic resonance (NMR) is used to study the resonance transition phenomenon between the Zeeman energy levels of magnetic nuclei. Both techniques share many common features in basic theory and experimental methods, such as the classical resonance process and resonance condition, the description of quantum mechanics, the theory of relaxation and the Bloch equation about the description of the macroscopic magnetization vector.

Since the ratio between Bohr magneton and nuclear magneton is equal to the mass ratio of a proton and an electron, i.e. 1836.15271, in the same magnetic field, the splitting of a nuclear Zeeman energy level is three orders smaller than that of an electron. So, the frequency range of occurring ESR falls in microwave band and ESR phenomenon can be observed under a weak magnetic field. According to the law of Boltzmann distribution, a large energy-level splitting results in a large particle population difference between the upper and the lower energy levels. Therefore, the sensitivity of ESR is higher than that of NMR. ESR can detect a sample of 10^{-4} mol. In addition, the paramagnetic relaxation interaction of electrons is much stronger than that of nuclei, as the electron magnetic moment is three orders larger than the nuclear magnetic moment. Except for radicals, the longitudinal relaxation time T_1 and transversal relaxation time T_2 are generally very short, so ESR spectral lines are generally wide.

Nonetheless, ESR can only investigate the local structural information within a few atoms that are related to unpaired electrons. Although ESR analysis on organic compounds has less advantage over NMR, ESR can be easily used to study solid materials. The greatest feature of ESR is that it is a direct method for the detection of unpaired electrons in substances so long as paramagnetic centers exist. Furthermore, if no unpaired electrons exist in an original sample, paramagnetic centers can still be created by means of adsorption, electrochemical, thermal, high energy radiation, chemical reactions, and so on.

C. Conditions for ESR

Based on atomic physics, the orbital angular momentum P_l and spin angular momentum P_s of an electron in atoms result in corresponding orbital magnetic moment μ_l and spin magnetic moment μ_s. So the total magnetic moment μ_j caused by the total angular momentum P_j is:

$$\mu_j = -g \frac{e}{m_e} P_j \tag{1}$$

where m_e is the mass of an electron, e is the electron charge, and g is a constant called Lande g-factor. The minus sign in eq. (1) represents the opposite direction between the total magnetic moment and the total angular momentum. Based on quantum theory, the Lande g-factor of a L-S coupling is:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{2}$$

where L and S are the quantum numbers of the total orbital angular momentum and the total spin angular momentum, respectively, summed from all electrons that have contributions.

From (2), if the atom magnetic moment is fully contributed by electron spin magnetic moment, i.e. L=0, S=J, then g=2; if completely contributed by electron orbital magnetic moment, i.e. L=J, S=0, then g=1; if contributed by both, then $1<g<2$. Therefore, the value of g depends on the specific structure of atoms. The determination of g-factor by experiment can explore the status of electron motion for the better understanding of atomic structure.

Normally, the unit of atomic magnetic moment is represented by Bohr magneton μ_B, so the electron magnetic moment in atoms can be written as:

$$\mu_j = -g \frac{\mu_B}{\hbar} P_j = \gamma\ P_j \tag{3}$$

where γ is called the gyromagnetic ratio, expressed as

$$\gamma = -g\frac{\mu_B}{\hbar} \tag{4}$$

Based on quantum mechanics, the spatial orientations of angular momentum P_j and magnetic moment μ_j are quantized in an external magnetic field and their projection components in the direction of the external magnetic field (Z-axis) are:

$$P_z = m\hbar \tag{5}$$

$$\mu_z = \gamma\ m\ \hbar \tag{6}$$

where m is the magnetic quantum number (m=j, j-1, …, -j).

If a paramagnetic substance with a non-zero atomic magnetic moment is placed in a constant external magnetic field B_0, the interaction energy is discontinuous as:

$$E = -\mu_j B_0 = -\gamma\ m\hbar B_0 = -mg\mu_B B_0 \tag{7}$$

The separation between adjacent magnetic energy levels is identical as

$$\Delta E = g\mu_B B_0 = \omega_0\hbar \tag{8}$$

If an AC electromagnetic field is applied in the direction perpendicular to the constant external magnetic field B_0, with a frequency of:

$$\omega\ \hbar = \Delta E \tag{9}$$

when ω=ω_0, electrons can transit between adjacent energy levels. By applying an AC magnetic field, the phenomenon of resonance absorption (or emission) between energy levels caused by the interaction between electron spin magnetic moment and external magnetic field is known as electron spin resonance. Equation (9) is the resonance condition, which can be rewritten as:

$$\omega = g\frac{\mu_B}{\hbar}B_0 \tag{10}$$

or

$$f = g\frac{\mu_B}{h}B_0 \tag{11}$$

For DPPH sample, the reference value of Lande g-factor is 2.0036. By substituting constants μ_B=5.78838263(52)×10^{-11} MeV·T^{-1} and h=4.1356692×10^{-21} MeV·s into equation (11), we get:

$$f = 2.8043B_0 \tag{12}$$

where the unit of B_0 is G (1 G=10^{-4} T) and the unit of f is MHz. If a microwave wavelength of 3 cm or frequency of 9370 MHz is used in the experiment, the required magnetic flux strength for resonance is 3342 G. Another necessary condition for resonance absorption is the particle number N_1 on a lower energy level should be higher than that on an upper energy level in an equilibrium state. Particle distribution obeys Boltzmann distribution under thermal equilibrium,

$$\frac{N_1}{N_2} = \exp\left(-\frac{E_2 - E_1}{kT}\right) \tag{13}$$

Since E_2>E_1, N_1>N_2, i.e. absorption transition (E_1→E_2) is dominant. As interactions and energy exchanges between spin magnetic moments or between spin magnetic moment and around particle (lattice) occur at any time, electrons on upper energy state can return to lower energy state, called relaxation. Due to this process, magnetic resonance absorption effect can continue over time. The required time for relaxation process is called relaxation time *T*, expressed by:

$$T = \frac{1}{2T_1} + \frac{1}{T_2} \tag{14}$$

where T_1 is called "spin-lattice relaxation time" or "longitudinal relaxation time" and T_2 is called "spin-spin relaxation time" or "transversal relaxation time".

D. Spectral Line Width

Similar to optical spectral line, ESR spectral line also has a certain line width. If a line width is expressed in frequency unit $\delta\nu$, then $\delta\nu=\delta E/h$ corresponding to an uncertainty δE of energy difference ΔE. According to the uncertainty principle, i.e. $\tau\delta E \sim h$ (τ is the lifetime of an energy level), we have:

$$\delta\nu \sim \frac{1}{\tau} \tag{15}$$

It means that a reduction of particle lifetime on upper energy level results in the widening of the associated spectral line. Particle lifetime reduction is caused by spin-lattice interactions and spin-spin interactions. For most free radicals, spin-spin interactions play a major role. This kind of interactions includes interactions between unpaired electrons and adjacent nuclear spins as well as interactions between unpaired electrons of two molecules. As a result, spectral line widening reflects the interaction information between particles, and is an important parameter in electron spin resonance spectroscopy.

Using a phase-shifted signal with an oscilloscope, a graph can be acquired and the full width at half maximum of an absorption peak, ΔB, can be determined as shown in Fig. 2. If the spectral line is a Lorentz-type, we have:

$$T_2 = \frac{2}{\gamma\ \Delta B} \text{ where } \gamma = g\frac{\mu_B}{\hbar} \tag{16}$$

Therefore, the transversal relaxation time T_2 of the resonance sample can be calculated.

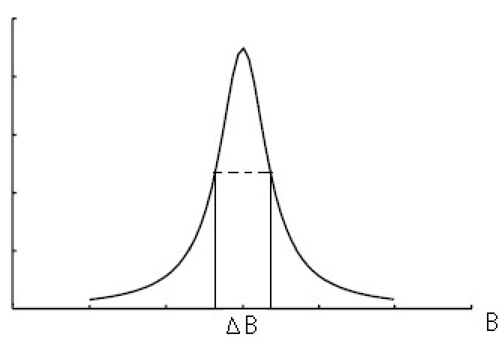

Figure 2 Calculation of transversal relaxation time based on absorption line width

E. Introduction to Microwave and Microwave Devices

(1) Microwave and its transmission

Commonly used microwave transmission devices include coaxial, waveguide, strip-line, micro-strip line, and so on. Hollow metal tube for guiding electromagnetic wave propagation is called a waveguide which is cylindrical with a rectangular cross section as shown in Figure 3. From electromagnetic field theory, an electromagnetic wave propagating in free space is transversal (TEM). Theoretical analysis indicates there are only two types of electromagnetic waves that can exist in waveguides: transversal electric (*TE*) wave (electric field having only transversal component and magnetic field having longitudinal component); and transversal magnetic (*TM*) wave (magnetic field having only transversal component and electric field having longitudinal component). In practice, waveguides are usually designed to guide only single waveform. TE_{10} wave is one of the simplest and the most commonly used waves, also called the primary wave.

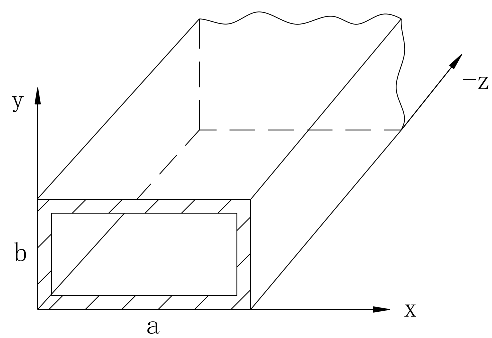

Figure 3 Rectangular waveguide

If a rectangular waveguide has a cross section of $a\times b$, and the tube is filled with a medium of dielectric constant ε and magnetic permeability μ, the propagating components of a TE_{10} wave along Z direction are:

$$E_y = E_0 \sin\frac{\pi x}{a} e^{i(\omega t-\beta z)} \tag{17}$$

$$H_x = -\frac{\beta}{\omega\mu}\cdot E_0 \sin\frac{\pi\cdot x}{a} e^{i(\omega t-\beta z)} \tag{18}$$

$$H_z = i\frac{\pi}{\omega\mu a}\cdot E_0 \cos\frac{\pi\cdot x}{a} e^{i(\omega t-\beta z)} \tag{19}$$

$$E_x = E_z = H_y = 0 \tag{20}$$

where $\omega=\beta\times(\mu\varepsilon)^{-1/2}$ is the angular frequency of the electromagnetic wave, and $\beta=2\pi/\lambda_g$ is called the phase constant,

$$\lambda_g = \frac{\lambda}{\sqrt{1-(\lambda/\lambda_c)^2}} \tag{21}$$

λ_g is called waveguide wavelength, $\lambda_c=2a$ is the cutoff or critical wavelength (a=22.86 mm and b=10.16 mm in this experiment), and $\lambda=c/f$ is the wavelength of electromagnetic waves in free space.

A TE_{10} wave has the following characteristics:

a. There is a cutoff wavelength λ_c, so only the electromagnetic waves with a wavelength $\lambda<\lambda_c$ can propagate in the waveguide.
b. Electric field vector is perpendicular to the wider wall of the waveguide (only E_y exists). Amplitude is zero at both sides along x direction, maximum at the middle, and uniform along y direction. Magnetic field vector exists in the plane of the wider waveguide wall (only H_x and H_z exist). Because the electric field of a TE_{10} wave has only transversal component, "1" represents one maximum value along the wider wall direction, and "0" means no change along the narrower wall direction (similarly, TE_{mn} means the electric field has m and n maximum values along the wider and narrower walls, respectively).

In practice, a waveguide is not infinite in length and a load is connected at the terminal. When the incident electromagnetic wave is not completely absorbed by the load, a reflected wave will exist in the waveguide so as to form a standing wave. A reflection coefficient Γ and a standing wave ratio (SWR) ρ are introduced to describe this state, as:

$$\Gamma = \frac{E_r}{E_i} = |\Gamma| e^{i\varphi} \tag{22}$$

$$\rho = \frac{|E_{\max}|}{|E_{\min}|} \tag{23}$$

where E_r and E_i are the incident and reflected waves at a specific cross section, respectively, φ is the phase difference between the two waves, $E_{\max}$ and $E_{\min}$ are the maximum and minimum values of the standing wave electric field, respectively. The relationship between ρ and Γ is:

$$\rho = \frac{1+|\Gamma|}{1-|\Gamma|} \tag{24}$$

If the incident microwave is completely absorbed by the load without reflection, it is called the matching state ($|\Gamma|=0$ and $\rho=1$) and the microwave in the waveguide is a traveling wave; if the terminal is an ideal conductor, a total reflection is formed ($|\Gamma|=1$ and $\rho=\infty$) yielding a standing wave state; if the terminal is an arbitrary load, partial reflection occurs yielding a traveling-standing wave state (or mixing wave state).

(2) Microwave devices

a. Solid state microwave signal source

Two types of microwave oscillators are commonly used, one is the reflex klystron oscillator and the other is a Gunn's diode oscillator, or known as a solid source.

The core of a Gunn's diode oscillator is a Gunn's diode based on the conductive band dual-valley structure (high/low energy valleys) of n-type gallium arsenide. In 1963, Gunn observed that, by applying a DC voltage to the two ends of an n-type gallium arsenide sample, sample current increases with an increase in voltage increasing when voltage is low; however, if the voltage exceeds a critical value, current decreases as voltage increases leading to a negative resistance effect. If the voltage continues to increase ($V>V_b$), the current tends to saturation as shown in Figure 4 indicating that an n-type gallium arsenide sample has a negative resistance characteristic.

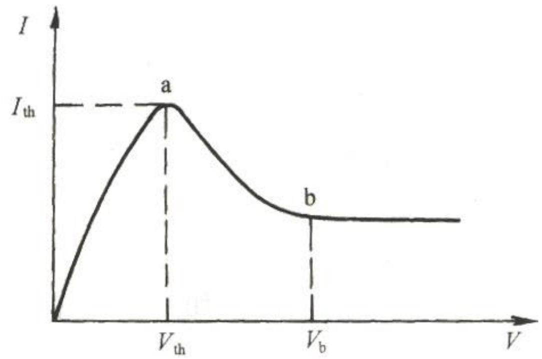

Figure 4 Current-voltage characteristic of Gunn's diode

The solid state microwave signal source used in this apparatus consists of a host electric unit, an oscillator and an isolator. The Gunn's diode is mounted in a waveguide resonant cavity of TE_{10} mode. By adjusting the micrometer of the oscillator, the insertion depth of the tuning rod into the waveguide cavity can be altered, thereby tuning the resonant frequency of the output microwave. Adjusting the tuning screw in the center of the flange in front of the waveguide cavity, an optimal coupling between the waveguide cavity and external waveguide circuit can be achieved. The isolator ensures the matching and isolation between the oscillator and the load and makes the microwave frequency and output power stable.

Through these press buttons on the panel of the host electric unit, the working mode of the oscillator can be selected as either equal-amplitude (i.e. continuous wave) or square wave. Working current or voltage is displayed on a 3-1/2 digits meter. The oscillator/isolator unit is connected with the host electric unit through a cable. **Warning:** Turn off electric power before connecting/disconnecting any cable to avoid damage to the electric control unit.

The frequency of the output microwave can be changed by adjusting the micrometer head. The frequency value can be determined from the micrometer reading by looking the "Comparison Table of Frequency-Micrometer Scale." In order to accurately determine the frequency of the oscillator, an external frequency counter or wavelength meter needs to be used.

If the microwave output is connected with a microwave detector, pressing down the "Square" wave mode button, the output of the detector will be square wave too when observed on an oscilloscope. If the output waveform is not a regular square wave, use a screwdriver to finely adjust the "Adj." screw on the front panel to achieve a satisfied square-wave output waveform. **(Note:** square wave has been preset in factory.**)**

b. Isolator

An isolator is an irreversible attenuator whose attenuation is very small in the positive direction (or the transmission direction) at about 0.1 dB or so, but very large in the opposite direction up to dozens of dB. The attenuation ratio of both directions is called isolation. If an isolator is mounted behind a microwave source, it has very little attenuation to the output power but very large attenuation to the reflected wave. Hence, the impact on the frequency and output power of a microwave source due to load variations is eliminated.

c. Magic tee

A magic tee (or magic T or hybrid tee) is a hybrid or 3 dB coupler used in microwave systems. Its structure is shown in Figure 5.

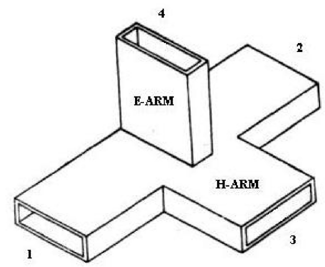

Figure 5 Structure of a magic tee

The magic tee is a combination of E and H plane tees. Arm 3 forms an H-plane tee with arms 1 and 2. Arm 4 forms an E-plane tee with arms 1 and 2. Arms 1 and 2 are sometimes called the side or collinear arms. Port 3 is called the H-plane port and port 4 is the E-plane port. A signal injected into the H-plane port will be divided equally between ports 1 and 2, and will be in phase. A signal injected into the E-plane port will also be divided equally between ports 1 and 2, but will be 180 degrees out of phase. If signals are fed in through ports 1 and 2, they are added at the H-plane port and subtracted at the E-plane port.

d. Crystal detector

Point contact diode (or microwave diode) is used in microwave detection systems with outer shell made of high frequency aluminum porcelain, as seen in Fig. 6. A crystal detector consists of a segment of waveguide and a microwave diode. Inserting a microwave diode between the two wide walls of a waveguide, detects the induction voltage between the two arms, which is proportional to the electric field strength.

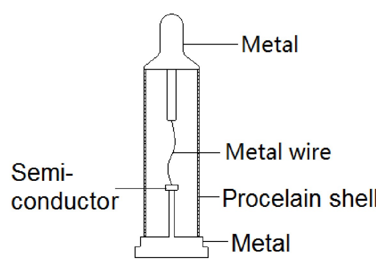

Figure 6 Structure of a crystal detector

e. Frequency meter

An "absorption type" resonance frequency meter is used in this experiment, which contains a hollow cylindrical cavity with a tuning micrometer marked scales. The hollow cavity is coupled to a straight waveguide through a hole to form a waveguide branch propagated by the microwave under test. If the cavity of the frequency meter is non-matching with the straight waveguide, the electromagnetic field in the cavity is weak and hence the cavity does not absorb microwave power (no impact on the microwave propagation in the waveguide). Under such case, the signal readout at the system terminal remains constant. By adjusting the micrometer to reach a matching state, a portion of the microwave power in the straight waveguide enters the cavity, leading to a reduction of the signal readout at the system terminal. When the detector reaches an absorption peak, the resonant frequency of the cavity is the microwave frequency, which can be determined from the micrometer reading through looking the "Frequency-Scale Table of 3cm Cavity Wavelength Meter"

f. Rectangle resonance cavity

A rectangle resonance cavity consists of a rectangle waveguide with a metal plate on the entrance (we call the plate as "Coupling plate"). The metal plate has a small aperture to allow the entrance of microwave to the waveguide. The other end of the waveguide is connected by a short-circuit piston to form a reflective resonance cavity. As the electromagnetic wave in the cavity forms a standing wave, the amplitudes of the electric and magnetic fields in the resonance cavity follow certain spatial distributions. In this apparatus, a narrow slit is opened on the wide side of the cavity. An experimental sample is placed in the cavity and can be moved along the cavity by a translation mechanism through the slit. The position of the sample can be read from the scale. When the sample is locating at the maximum amplitude of the field, resonance absorption peak will be observed.

g. Short-circuit piston

A short-circuit piston that is attached to the terminal of a transmission system is a single-arm microwave device, as seen in Fig. 7. It has no influence on the incident microwave power as it fully reflects microwave power without absorption to form a standing wave in a transmission system. It is a rectangle waveguide with a movable metal short-circuit end that can be adjusted with a micrometer. In this apparatus, a short-circuit piston and a rectangular resonance cavity form an adjustable rectangular resonator.

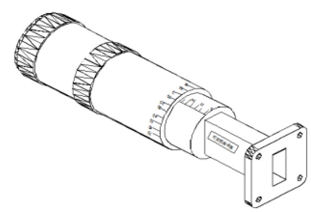

Figure 7 Structure of a short-circuit piston

h. Single stub tuner

A transmission line that is terminated with a load impedance equal to the characteristic impedance Z_o of the line will not reflect an incident wave at that point, and the transmission line is said to be impedance matched. However, a transmission line that is terminated with a load impedance different than Z_o will reflect part of an incident wave back toward the generator. Reflections are often undesirable and should be eliminated. If the load impedance has a nonzero real part, it is possible to eliminate the reflection by placing a proper length of transmission line (the stub) at the right place. A properly located stub of the proper length combines with the load impedance to yield equivalent impedance equal to Z_o, and thus impedance matches the transmission line at the point where the stub joins the main transmission line. This procedure is known as single stub tuning or stub matching. Stub tuning can give impedance matching only at a single frequency.

3. Working Principle and Specifications

This experimental system of microwave electron paramagnetic resonance works in the three-centimeter band (frequency near 9370 MHz). An adjustable rectangular resonant cavity is used with the system block diagram shown in Figure 8.

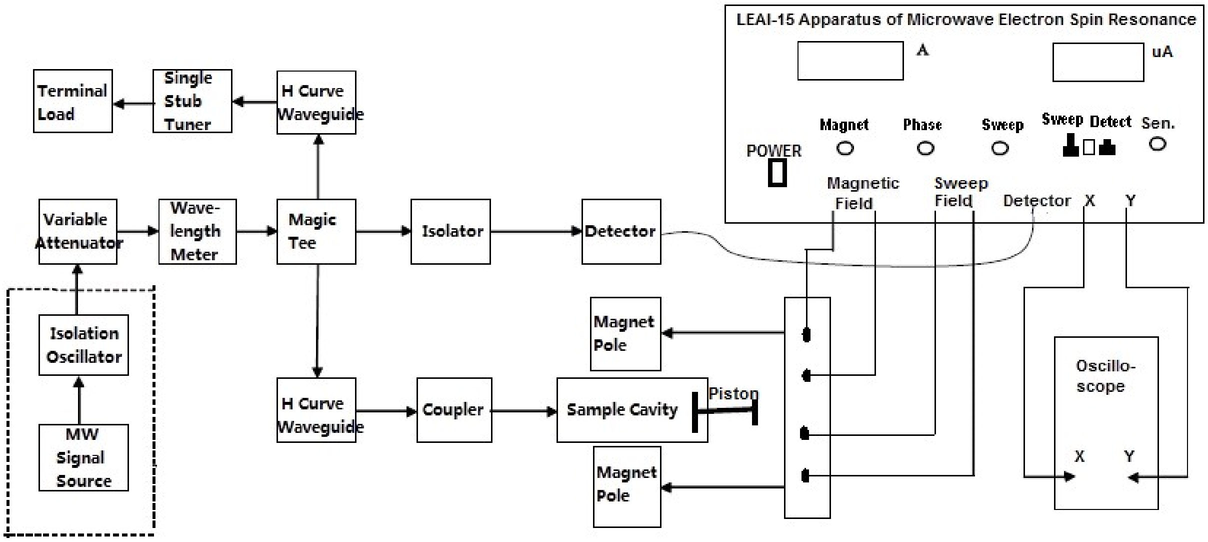

Figure 8 Block diagram of the experimental system

The microwave signal source provides a microwave signal at ~9370 MHz. Through isolator, attenuator, and wavelength meter, the microwave signal is equally divided into two portions by the magic tee. In one arm, the microwave signal enters the adjustable rectangular sample resonance cavity whose length can be changed with a movable piston at the end of the rectangular cavity. To ensure that the sample pre-installed in the cavity locates at the maximum point of the microwave magnetic field strength, a narrow slit is opened in the middle of the wide side of the resonant cavity. Through a mechanical actuator, the sample can be placed at anywhere in the resonant cavity. The position can be read out from the scale on the side. The experimental sample is organic free radical DPPH sealed in a glass tube.

"X" port of the main unit provides a synchronization signal for oscilloscope. Adjusting "Phase" knob allows the two resonance absorption peaks of the negative half and the positive half sine wave scanning to be overlapped. When using an oscilloscope, the scan signal is the 50/60 Hz sine wave output from the main unit, and Y-axis is the microwave signal from the detector. Substituting magnetic field strength B and microwave frequency f into the magnetic resonance condition equation (11), the Lande's *g*-factor can be derived.

By using the adjustable rectangle resonant cavity, the following experiment can be conducted: adjusting the location of the short circuit piston and making the length of the resonant cavity length about 134 mm, placing the sample at the middle point; next, adjusting the magnetic field while observing electron resonance absorption signal on the oscilloscope. Remain the short circuit piston location unchanged, move the sample by distance *s* until the electron resonance absorption signal occurs again. Distance *s* is a half of the microwave wavelength, i.e. $\lambda_g/2$.

Main specifications

Microwave System:	
Short-circuit piston	adjustment range: 30 mm
Sample	DPPH powder, tube dimensions: ϕ2×6 mm
Microwave frequency meter	measurement range: 8.6 GHz ~ 9.6 GHz
Waveguide dimensions	inner: 22.86 mm × 10.16 mm